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TRANSLATION

GLASSY STATE
(SELECTED ARTICLES)

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GLASSY STATE (SELECTED ARTICLES)

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FTD-TT- 63-265/1+2+4 Date 6 May 1963

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FORMATION OF THE CRYSTAL PHASE FROM A SILICATE FUSION

A. I. Avgustinik

In previous works [1] we hypothesized the possibility of the existence in a silicate fusion of stoichiometric formations which are the primary product of the reaction between components of this fusion. We assumed that these formations are the product of an incomplete inhibited reaction not having phase characteristics. From these formations, under favorable conditions, a new phase occurs in the form of crystal seeds.

As long as the required thermodynamic conditions (temperature, pressure, concentration of components) are absent, and conditions conducive to the formation of new phases (crystal seedings, gas bubbles) are not created, the reaction will be inhibited and, on cooling, the fusion will congeal into a solid glass. During cooling, however, the fusion will not remain unchanged. The above-mentioned stoichiometric formations develop in it; these increase in size when the temperature is slowly lowered. We called these formations the pre-seeding groups, p-groups for short. The pre-seeding groups can be represented as the specific form of A. A. Lebev's crystallites.

In our first report [1,2] we showed the possibility of calculat the dimensions of such p-groups, if we use an equation analogous to W. Thomson's vapor-condensation equation. The calculated dimensions of the p-groups (their radii) in molten quartz are shown in Fig. 1. As can be seen, as the temperature drops the dimensions of the groups increase from 90 A at 1980°K to 250 A at 1270°K.

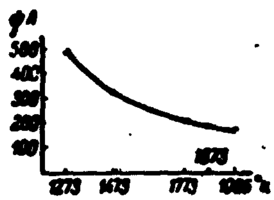

Fig. 1. Change in dimensions of the cross section of p-groups in a quartz fusion vs. temperature (calculated).

For experimental proof of the existence of p-groups as a primary product of the reaction in a silicate fusion we investigated (jointly with Ye. Oshkaderovaya) the crystallization of a fusion which corresponds to the composition of lithia mica — taeniolite $2MgO \cdot 4SiO_2 \cdot KF \cdot LiF$. The low fusion temperature (1210°) of this compound is very convenient for our purposes.

The formation of taeniolite crystals was monitored by ionization x-ray analysis (tube BSV-4 with a nickel filter, U = 28 kv, i = 22 ma), and also by microscope.

For all glasses subjected to various heat treatment (up to and including samples with incipient crystallizations) infrared absorption spectra were simultaneously obtained, for which we used the IKS-12 infrared spectrophotometer.

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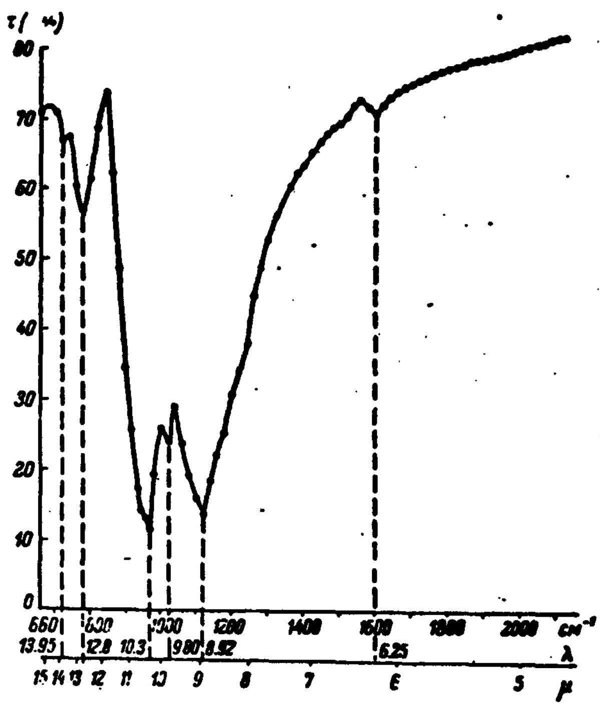

Fig. 2. Taeniolite absorption spectrum in the infrared region at wave lengths from 4.5 to 15μ.

As the starting materials we used chemically pure KNF_2, Li_2CO_3, MgO, and roasted rock crystal ground in jasper mortar until it completely passes through a sieve with 4900 openings per cm^2. The batch was fused in a platinum crucible under two sets of conditions providing good and poor melting of the batch: at 1500° for 1 hour and at 1350° for 15 min. The glass fused at 1350° was at once subjected to reduced temperatures for p-groups to develop and crystal seeds to form. The following regimes were used: 2 hours at 1140°, 2 hours at 1120°, and 10, 25, and 30 minutes, and 3 hours at 1100°. The state of the fusion was fixed by rapid cooling, by immersing the crucible with the fusion into water.

Slight turbidity, indicating crystal seeds, was noticed only after 30 minutes at 1100°. We were unable to detect the crystal phase by ionization x-ray analysis in glass kept at 1140 and 1100°; the glass remained transparent. Taeniolite was completely crystallized when kept for 3 hours at 1100°.

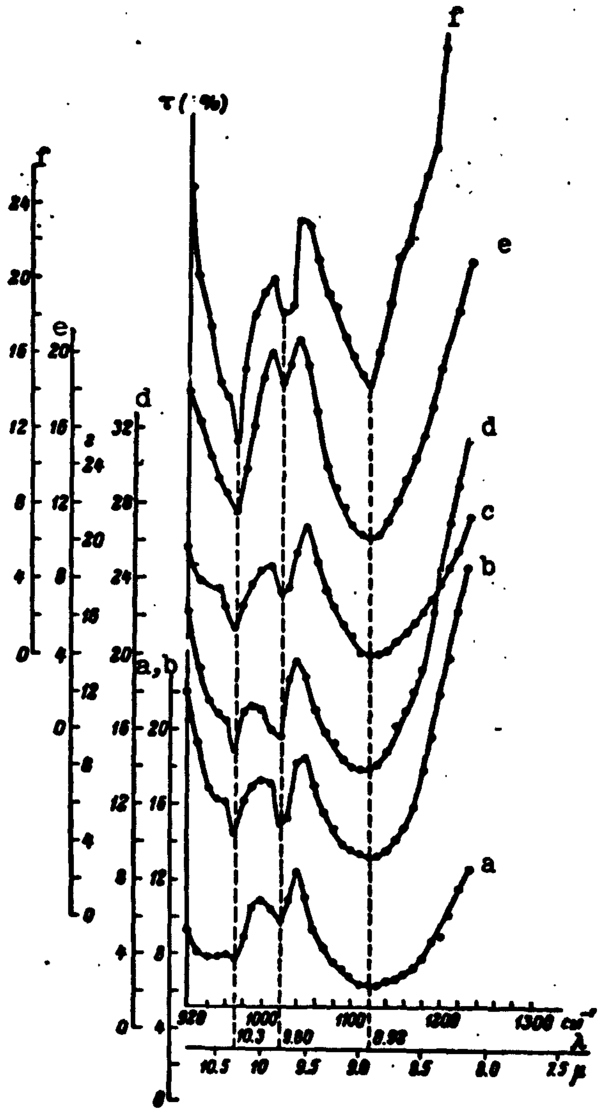

Fig. 3. Absorption spectra of glass of taeniolite composition under various conditions.
a) at 1500°, 1 hr. b) at 1350°, 15 min., c) at 1100°, 10 min., d) at 1100°, 25 min., e) at 1100°, 30 min., f) at 1100°, 3 hrs.

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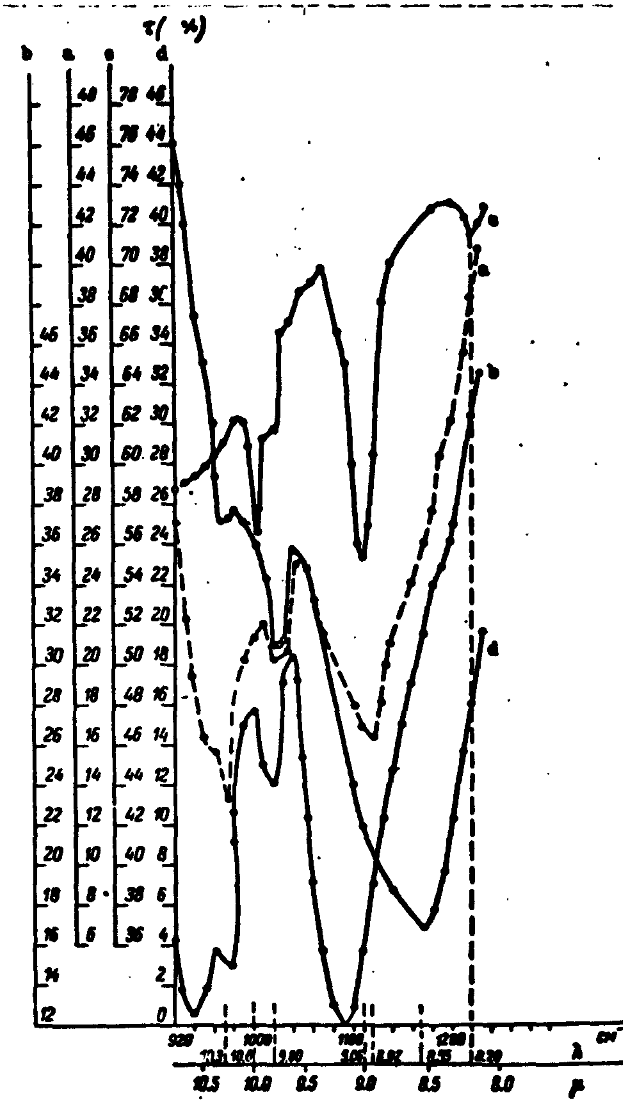

Fig. 4. Comparison of the spectra of the crystal absorption of: a) taeniolite, b) clioenstatite, c) quartz, d) magnesium oxide.

On the taeniolite spectrograms there are absorption bands in the region of wave lengths 4.5-15μ, namely at 6.25, 8.92, 9.80, 10.3, 12.8, and 13.95μ (Fig. 2). The most characteristic bands are in the region of 8-11μ. The spectrograms of glass held at different temperatures were the same in this region.

Special experiments revealed a satisfactory reproduction of the spectrograms obtained for the investigated glass.

The basic results of the investigation are shown in the series of spectrograms in Fig. 3. The reaction among the starting components with taeniolite formation occurs very rapidly, which is evident from spectrograms a and b obtained for glass fused at 1500° (baking time 1 hr.) and at 1350° (baking time 15 min.) and not subjected to heat treatment. The observable absorption bands — 8.92, 9.80, and 10.3μ — correspond precisely to the crystal bands although they were obtained for completely transparent glass giving an x-ray photograph characteristic of the vitreous state. These results lead to the conclusion that in the glass there exist some groups which do not appear as an independent phase but at the same time have the same chemical bonds at taeniolite crystals.

For glass which has been kept at 1100° (curve b, 10 min.; curve c, 25 min. in Fig. 3) the position of the absorption bands remains unchanged, but their intensity increases somewhat. After 30 minutes at 1100°, when slight turbidity appears in the glass, a significant change in the intensity of the absorption bands appears on the spectrograms; these bands now become similar (with respect to intensity and position) to the spectrogram of the taeniolite crystal.

The results of the investigation allow us to conclude about the existence, in a fusion and then in glass which corresponds to the composition of taeniolite, of groups which are characterized by the same chemical bonds as in the taeniolite crystals themselves. However, unlike the crystals, the emerged formation (p-groups) do not have phase characteristics: interfaces and constant parameters, which characterize the crystal lattice. The existence of these p-groups still does

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not complete the chemical reaction between fusion components; it becomes completed when conditions are created for the development from p-groups of crystal phase seeds of the same composition.

To assure that the spectrograms of the investigated glass do not reflect other compounds which can exist here, e.g., clinoenstatite, which forms as a result of the reaction between MgO and SiO_2, and also unreacted quartz and magnesium oxide, spectrograms of similar preparations were recorded (Fig. 4). As is evident, the taeniolite spectrogram (a) is not similar to the spectrograms of clinoenstatite (b), quartz (c), and magnesium oxide (d), and the absorption band 8.92 is not repeated in any of the other preparations.

In conclusion, I wish to thank V. A. Florinskaya with whom the obtained spectrograms were discussed.

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INFRARED REFLECTION SPECTRA OF SODIUM-SILICATE GLASS, AND THEIR CONNECTION WITH STRUCTURE

V. A. Florinskaya

The best way to understand glass structure is by successive investigation of the whole transition process: mixture — fusion — glass — crystal. For this purpose, under industrial conditions, 25 glass specimens of the system Na_2O-SiO_2 with various Na_2O content were fused in large quartz vessels. During melting we removed specimens every 30-40 min; these abruptly hardened in the air. At the same time, thin films were blown from the fusion. From uniform pieces of potter's glass we prepared discs which had an optical finish. The latter were crystallized in ovens at a uniform temperature.

Figure 1 shows the reflection spectra of a sodium disilicate glass at various periods during its existence.

If we assume that in the silicate lattice of glass the SiO_4 tetrahedra are arranged chaotically and the sodium ions are distributed purely statistically, then in the region of the first intense reflection band at 9-11 μ we should have a collection of all possible frequencies (from isolated tetrahedra frequencies to frequencies characteristic of the skeleton). The spectrum in this region would

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be depicted as a diffused curve with a single maximum shifted somewhat toward long waves relative to the strongest maximum selective reflection of the corresponding crystal silicate. Actually, the spectra of alkaline two-component glass often have the form, shown in Figs. 1-7. In the region where only the first strongest band of selective reflection can lie, instead of a single band, as is usually the case with sodium crystal silicates, there are two bands. For instance, a comparison of curves 6 and 1 of Fig. 1 shows that in the region 9.6-9.8 μ, where there is the most intense peak of reflection of the laminated sodium disilicate, minimum reflection is observed in the glass spectrum, whereas strong bands of approximately equal intensity appeared significantly shifted in various directions. Such a spectrum form is contrary to Zachariasen's hypothesis. There are at least two types of atomic groupings in the glass: with a very high degree of tetrahedra connection (band at 9.1-9.2 μ) approaching that of high-temperature cristobalite, and with a low degree of tetrahedra connection (band at 10.5-10.6 μ)*, i.e. the sodium disilicate in the glass under consideration is dissociated to a significant degre We can consider that the structure of this glass, in the first rough approximation consists of regions with high silica content (regions of free silica in the form of cristobalite crystallites, and regions of high-silicic compounds)** and regions with high sodium content.

*The second, fundamental band in the region 12-13.5 μ in the reflection is weak; therefore we did not consider it.

** The relation between the silica quantity and high-silicic compounds, depending on the history of the glass, can be changed; as a result, the band peak can be shifted.

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There can be many other intermediate atomic groupings in the glass, including sodium disilicate crystallites, but in the present case these two groupings are predominant.* Researchers, adhering to Zachariasen's hypothesis, attempt to explain the presence of a doublet in the sodium-silicate glass spectrum by the appearance of dual type bonds: Si-O-Si and Si-O-Na, which cause bands at 9.1-9.2 and 10.5-10.6μ, respectively. This explanation should not be recognized since there are Si-O-Si and Si-O-Na bonds in the crystal silicate lattices, particularly sodium disilicate.

It has been previously reported**, however, that there can be three types of various spectra of crystallized glass of this composition, not one of which resembles the spectrum of the glass under consideration. Besides this, as is apparent from Fig. 5, the spectra of the same glass composition can differ substantially. Hence, the factors determining the spectra form are not simply the Si-O-Si, and and Si-O-Na bonds, but the structure of the lattice in which this bonding occurs. Crystallized glass, of sodium disilicate composition or near to it, can have spectra, similar to curve 1 in Fig. 1. This is the case, however, when we deal with a mixture of silica (or high-silicic silicate) with heavy sodium silicate. Figure 4 of the previous report shows such spectra.

*That is, curve 1 can be considered as the result of the superposition of the spectra of a number of atomic groupings of different structure among which there are some predominant ones.
** See p.157 of original text.

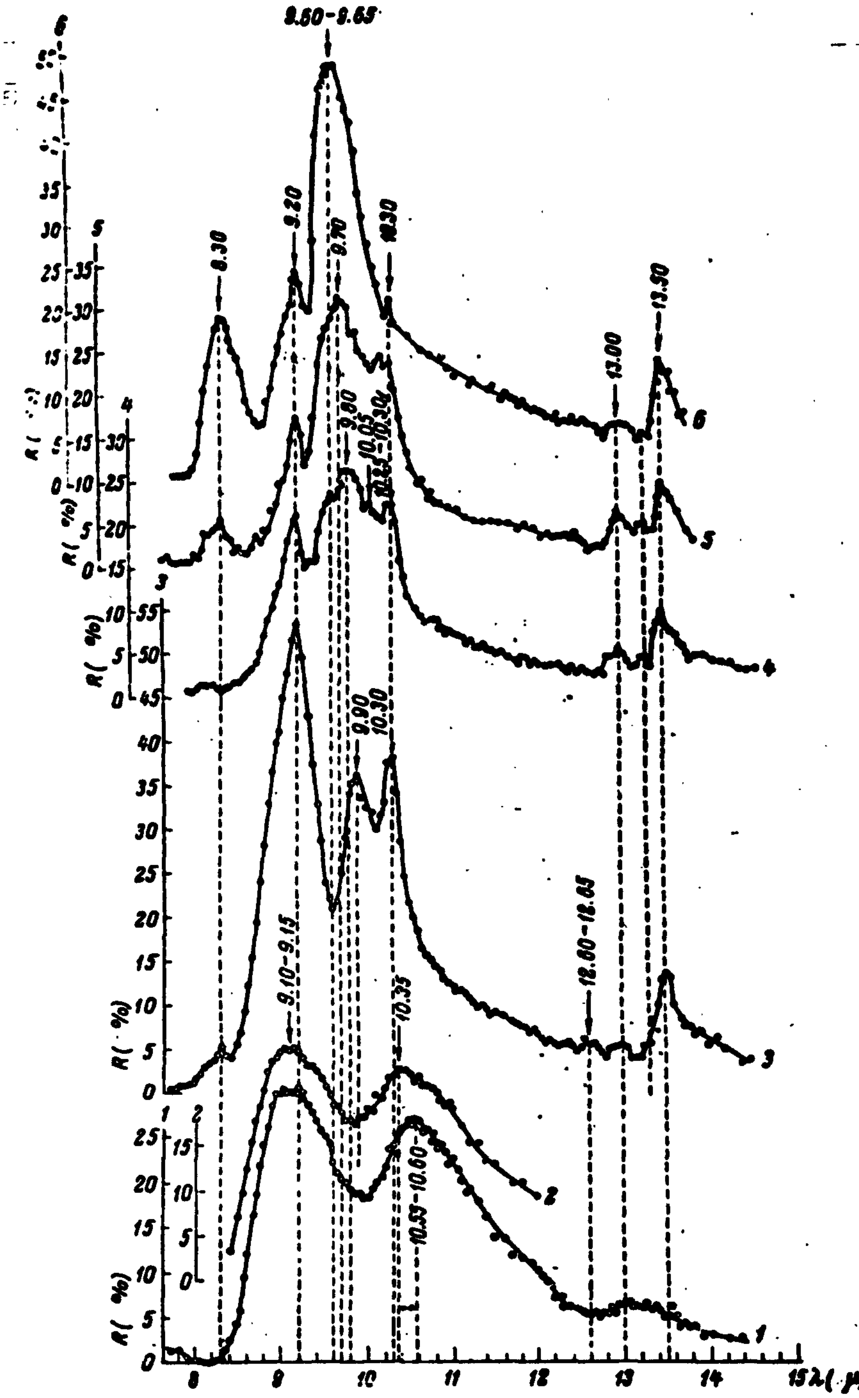

Fig. 1. Glass reflection spectra with 33.3% Na_2O and 66.7% SiO_2 (fusion No. 1000). 1) original glass; 2) crusty part of the rich glass heated at 620°, τ = 1 hr; 3) crusty part of the completely crystallized glass at 620°, τ = 144 hrs; 4) the same, τ = 576 hrs; 5) the same, τ = 1166 hrs; 6) subcrustal part of the specimen crystallized at 800°.

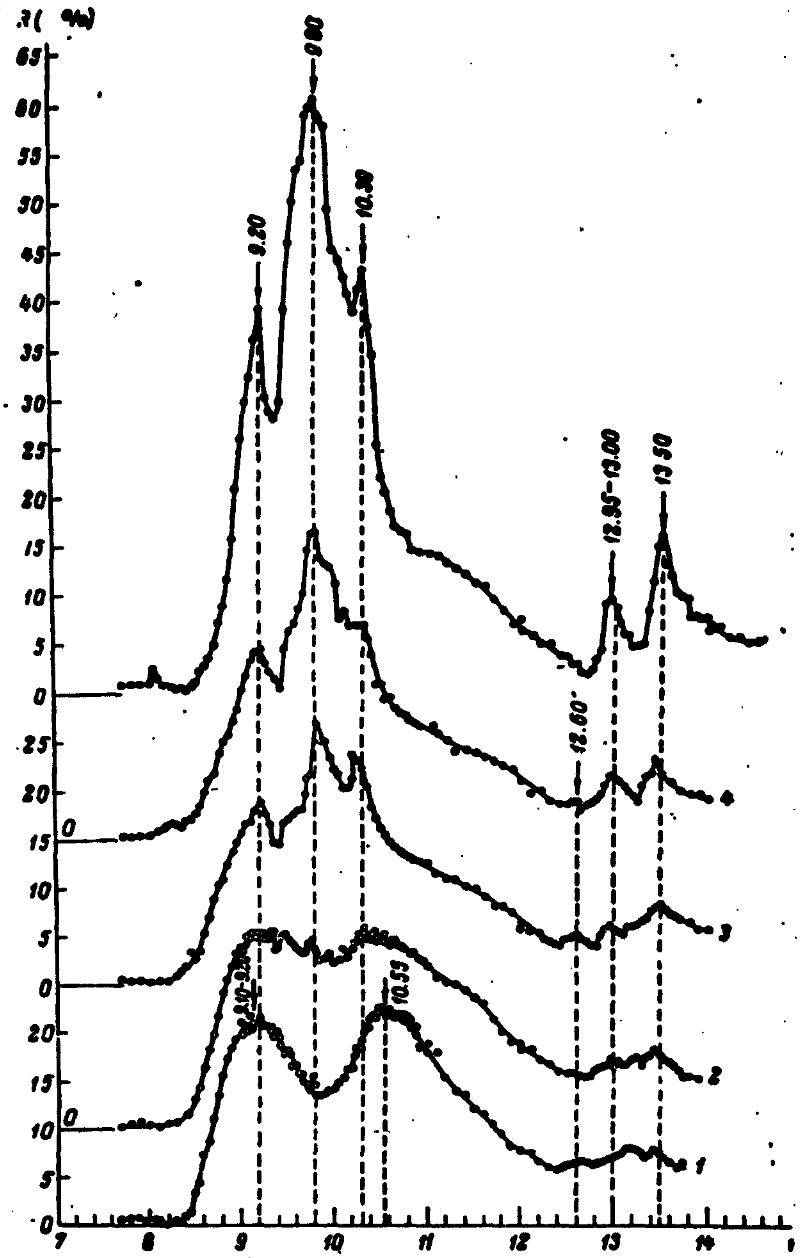

Fig. 2. Glass reflection spectra with 33.3% Na_2O and 66.7% SiO_2 (fusion No. 1772). 1) initial glass fused in a 100-liter quartz vessel; 2) crusty part of the glass heated at 620°, τ = 1 hr; 3) the same, interrupted (fog), τ = 3 hrs; 4) without interruptions (fog), τ = 3 hrs; 5) the same (crystallized glass), τ = 6 hrs.

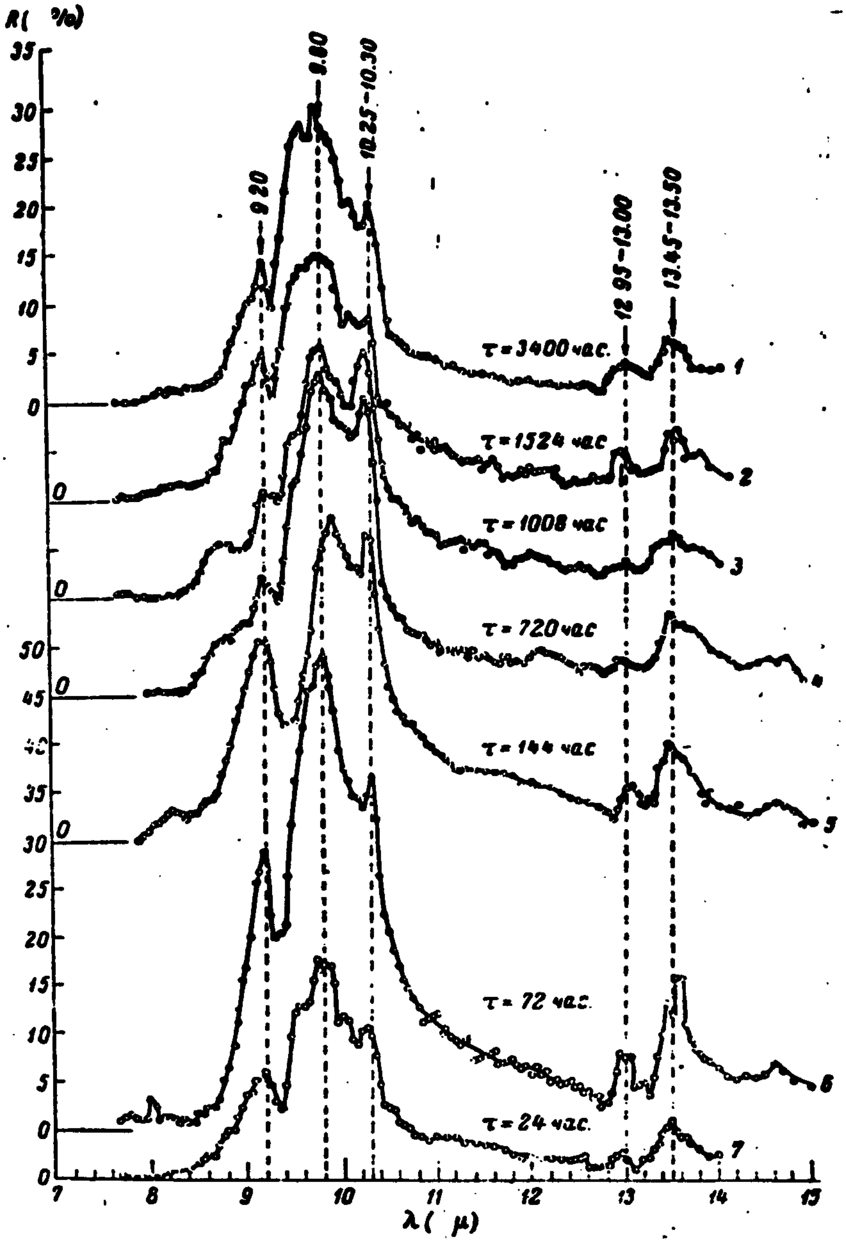

Fig. 3. Reflection spectra of the crusty parts of the crystallized glass with 33.3% Na_2O and 66.7% SiO_2, heated at 620° from 24 to 3400 hrs. (melt No. 1772).

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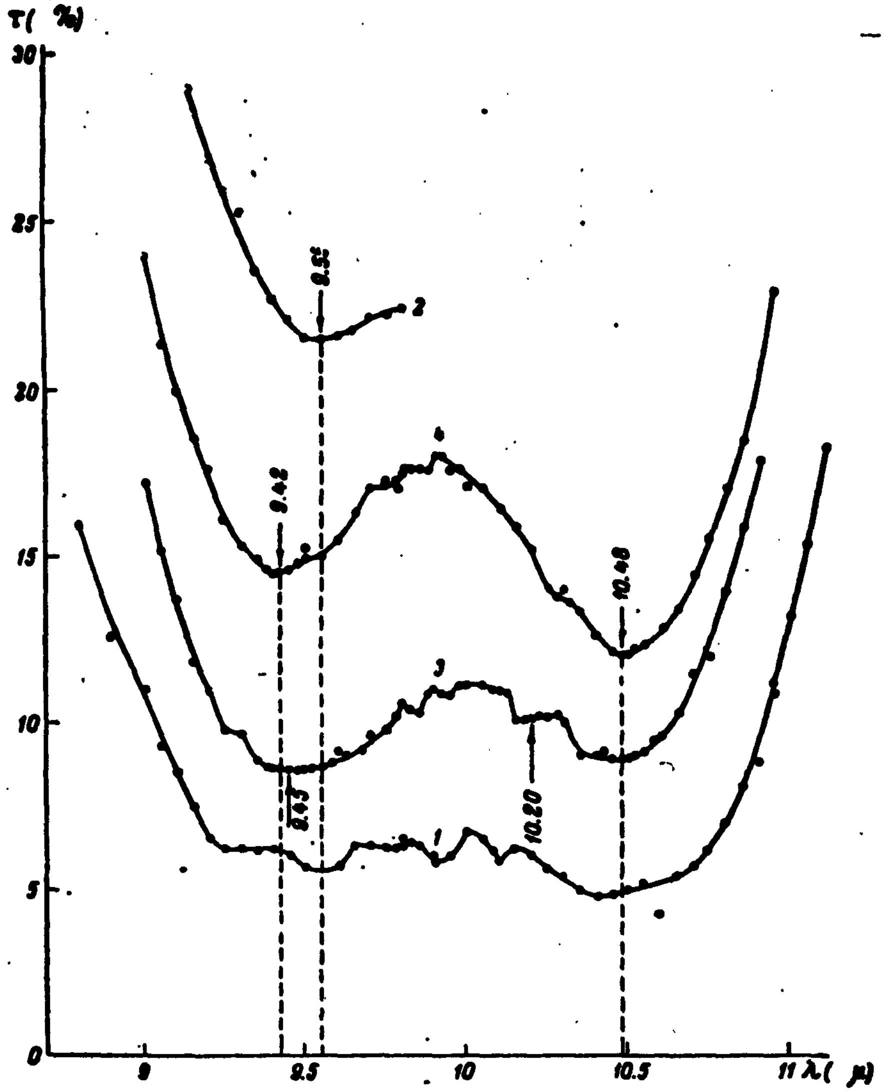

Fig. 4. Transmission spectra of film blown from a glass fusion with 33.3% Na_2O and 66.7% SiO_2 at various temperatures. 1) thick film blown from a fusion at 1450°; 2) thin film blown from a fusion at 1450°; 3 and 4) films blown from a fusion at 1080°.

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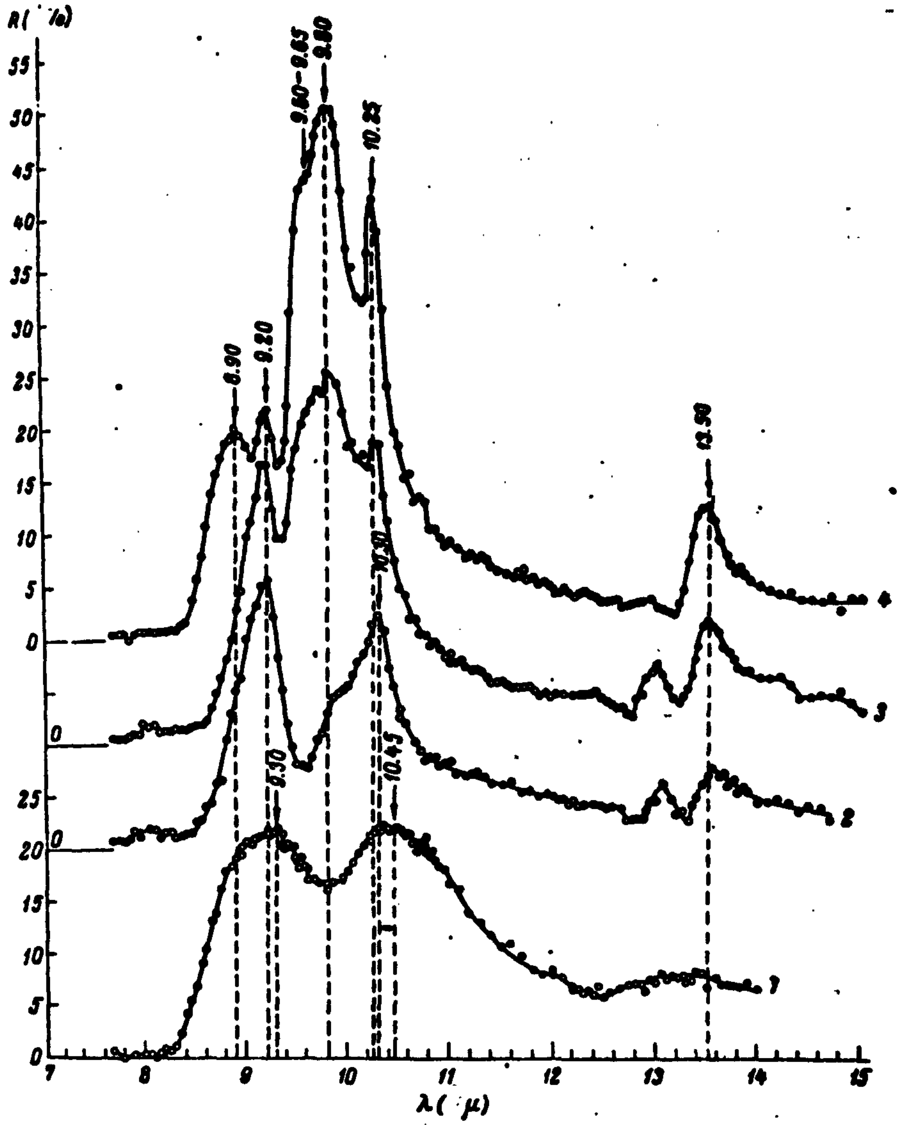

Fig. 5. Reflection spectra of glass with 30% Na_2O and 70% $2SiO_2$. 1) initial glass fused in a 100-liter quartz vessel; 2) crusty part of completely crystallized glass heated at 620°, τ = 576 hrs; 3) same, τ = 720 hrs; 4) same, τ = 1008 hrs.

To crystallize sodium disilicate from glass having a spectrum similar to curve 1, Fig. 1, two processes are necessary: 1) synthesis between silicate-rich and rich-sodium-components; 2) formation of the crystal lattice. These two processes can be divided in time.

Here two cases are possible.

1. The rate of glass crystallization is much faster than a chemical reaction brought about by sodium ions diffusing from high sodium content regions into sodium-poor regions. In this case, at the start of crystallization crystals precipitate whose structural rudiments (crystallites) are already in the initial glass (or were created in the heated glass only as a result of partial but not radical rearrangement of these atomic groupings in the initial glass) and the reaction, during which sodium disilicate forms, is already occurring in the solid crystalline phase.

Figure 1 shows such a case. After an hour of heat treatment the first band at 9.10-9.15 μ maintains its position and the second band at 10.55-10.60 μ shifts somewhat toward the first, i.e., atom groupings causing the second band to appear in the glass spectrum are partially rearranged. After 144 hrs cristobalite crystallizes in a significant amount (peaks at 8.30, 9.15-9.20, and 12.6-12.7 μ); its structure is different from low-temperature cristobalite; in addition, the silicate with a large sodium content crystallizes and its principal peak position (10.3 μ) is nearly the same as sodium metasilicate (10.20-10.25 μ) and [2] orthosilicate (10.3 μ); also an unstable silicate (peak at 9.90 μ) is precipitated as a result of partial reaction between the silica and heavy sodium silicate. After 576 hrs the amount of silica in the crystallized glass decreases sharply, the amount of heavy silicate also decreases, and an intermediate silicate evolves. Thus, a new silicate is developed with reflection peak at 9.80 μ. After a while the latter is also reorganized into a silicate similar to the one which crystallized at 800°; however, even after heat treating for 1166 hrs this process is not complete.

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2. The rate of glass crystallization will be less than or equal to the rate of the chemical reaction between silica-rich and sodium-rich components. In this case a new chemical compound starts to form in the vitreous state and during crystallization precipitates as a first phase. Figures 2 and 3 show crystallization of glass of a sodium disilicate composition*. After heat treating an hour, the specimen was for the most part glass, after 3 hours the first crystalline fog formed on its surface, and all the remaining specimens had been completely crystallized.

Figure 4 shows the transmission spectra of two batches of films blown from a glass fusion at 1450° (before agitating the glass) and at 1080° (before removing the pot from the oven). The transmission of the film was measured on a Beckmann spectrophotometer. Curves in Figs. 2 and 4 point out that, as in the previous case, the glass structure is heterogeneous, and this heterogeneity already occurs in the fusion. On heat treating the glass, a chemical reaction** starts between silica-rich and sodium-rich components; therefore after treating an hour both hands converge at 9.80 μ where the minimum is observed in the spectrum of the initial glass, and in the spectrum of the heated glass the reflection coefficient starts to increase. The laminated sodium disilicate, whose peak of selective reflection is at 9.80 μ, precipitates as the first phase upon further treatment.

Figures 5 and 6 show two different cases of the glass crystallization process with 30% Na_2O of one and the same fusion. Curve 2,

*Glass was melted in a 100 liter quartz pot.

**If some sodium ions leave the sodium-rich regions, then the reflection band which corresponds to these groupings must shift toward the short wavelengths since the band shifts to the short-wave side with a decrease of sodium content in the crystallite silicate.

Fig. 6 pertains to rich glass. From Fig. 5 we can see that the structure of the glass under consideration is heterogeneous. There are both regions of high silica content (band at 9.3 μ) and regions with high Na_2O content (band at 10.5 μ). The curves of film transmission (Fig. 7) indicate that there are silica regions in the glass (crest at 9.3 μ), high-silica silicates (peak at 9.5 μ), sodium disilicate (peak at 9.8 μ), and silicates with a high Na_2O content (peak 10.4 μ). This glass can also be crystallized by another method. In one case, cristobalite and an unknown sodium silicate, whose rudimentary structure (crystallites) was already in the glass, at first crystallized on the glass surface. Figure 5 shows such a case. The spectrum of glass heated for 576 hrs is a superposition of the silica and the heavy sodium silicate spectra. In the solid phase these substances are already chemically interreacting and as a result sodium disilicate (peak 9.8 μ on curves 3 and 4, Fig. 5) is gradually formed. This is a very slow reaction. In another case silica-rich and sodium-rich components synthesize significantly faster, which causes the sodium disilicate to immediately precipitate as the first phase. Figure 6 shows such a case.

Curve 3, Fig. 7 shows the transmission spectrum of a film blown from a fusion of another glass melt (also melted in a 100-liter pot). This spectrum shows that the same synthesis had already begun in the glass fusion.

Figures 8 and 9 show the change of the reflection spectra of glass with 25.5% Na_2O* (the composition of the eutectics between the silica and sodium disilicate) during its lifetime.

Curve 3, Fig. 9 is a spectrum of the subcrustal part of a

*Glass was melted in a 100-liter quartz pot.

crystallized specimen heated for 267 hrs at 620°. The spectra of the subcrustal part of all completely crystallized glass heat treated for 60-1008 hrs have a similar form. From Fig. 8 we can see that the structure of the fusion is heterogeneous in the earliest period. In it there are both high silica content regions (band at 9.2 μ) and sodium-rich regions (band at 10.4 μ). Upon subsequent holding of the fusion at 1450°, the heterogeneous components begin to synthesize, resulting in partial bonding of the silica and loading, on the one hand, to the formation of high-silica compounds and, on the other hand, to the formation of silicates with a smaller Na_2O content as compared to the previous case. Therefore both hands are somewhat shifted. Some sort of very primitive silica (band at 9.2 μ on curve 5) and some sort of sodium silicate with a large Na_2O content, whose structural rudiments were already in the fusion at first precipitated on the glass surface on crystallization at 620°. Upon further heat treatment both compounds chemically interacted, whereupon the reaction developed toward the formation of the same compound which is a basic part of the crystallization product of internal parts of the specimen (peak at 9.5 μ on curve 3, Fig. 9). In the solid phase this reaction is even slower than in the case of glass with 33.3 and 30 % Na_2O and is not complete after 1812 hrs. Likewise, crystallization occurs at higher temperatures, including temperatures close to liquidus. This is obvious from Fig. 10 which shows the reflection spectra of the crustal parts of glass crystallized at various temperatures. The eutectic mixture between silica and the sodium disilicate is not formed immediately. The sodium disilicate does not form until later as a result of the chemical reaction between the silica and heavy sodium silicate.

The process of glass crystallization at 620° occurs differently in the subcrustal parts of the specimen. Here the growth rate of silica crystals and the heavy sodium silicate, whose structural rudiments were already in the glass, is significantly less than on the surface. The diffusion rate of sodium ions is greater than the growth rate of the above-mentioned crystals, consequently the chemical reaction between sodium-rich and silica-rich components has time to occur which results in the crystallization of another compound in the internal layers. This conclusion is confirmed by an investigation of the reflection spectra of the crustal parts of glass heat-treated at 570°. The crystallization rate at this temperature is very small, therefore even after 12 days of heat treatment only a thin crystalline crust of the order of 3 mm thick had time to form on its surface and the remaining part is glass. Since the crystallization rate is less than or comparable with the chemical reaction rate, then a compound whose spectrum is similar to curve 3, Fig. 9 is immediately formed on the specimen surface as is shown in Fig. 10.

Figure 11 shows transmission spectra of films with 50% Na_2O (different melts) blown from a glass fusion.

Figure 12 shows reflection spectra of glass with 50% Na_2O (same melt to which curve 1, Fig. 11 pertains) at various periods of its life. A comparison of reflection and transmission spectra of glass with the sodium metasilicate spectrum (peak at 10.2μ on curve 3, Fig. 12) [1-4] shows that the bulk of the compound Na_2O SiO_2 is dissociated in the glass. The structure of the fusion and glass is basically made up of formations of a dual nature. Some of them have been enriched by silica and have a high degree of coupling of SiO_4 tetrahedra approaching that of the laminated sodium disilicate (band at 9.6 μ) or to the degree of coupling in more silicic compounds

[2,4]. Others have been enriched by Na_2O and do not have direct intercoupling of SiO_4 tetrahedra, since the band has shifted to the long-wave side even with respect to orthosilicate. If we crystallize such a glass so quickly that the sodium ions do not have time to diffuse from sodium-rich regions to sodium-poor regions, then we could crystallize out crystals of less than and more than 50% Na_2O content. Experience shows that we can actually crystallize out such crystals on the specimen surface where the crystallization rate is very high. This is obvious when we compare curves 1 and 2, Fig. 12. At first a laminated sodium disilicate (band at 9.6 μ) and crystals with a large sodium content (band at 11 on curve 2) crystallized on the surface. Further, they interract in the solid phase, which, all things considered, results in the forming of a sodium metasilicate (band at 10.2 μ on curve 3).

Summing up, we can consider that the systematic experimental material obtained on the high-grade glass confirms the heterogeneity of glass microstructure and the presence of zones having an ordered atom distribution — crystallites.

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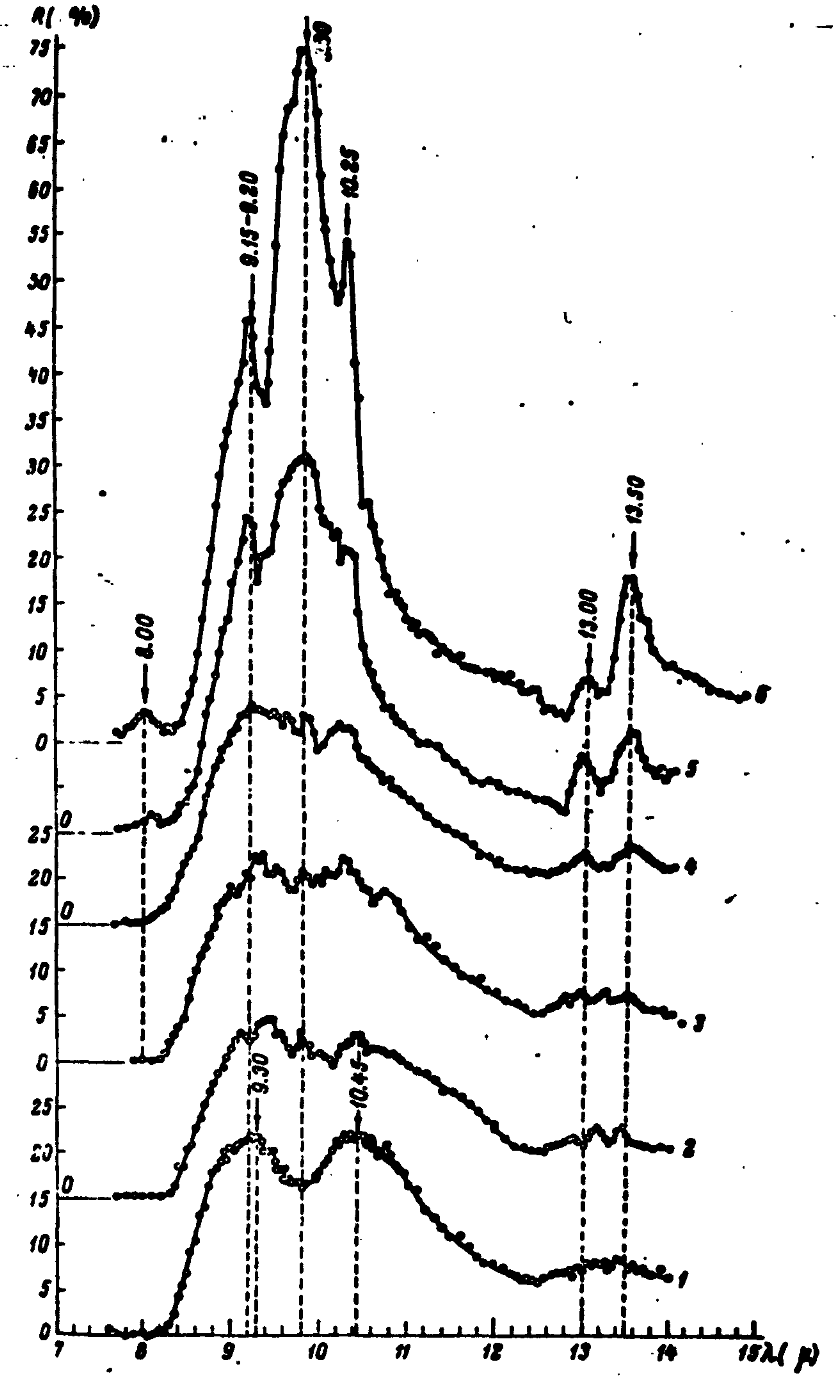

Fig. 6. Reflection spectra of glass with 30% Na_2O and 70% SiO_2. 1) initial glass; 2) crustal part of rich glass heated at 610-620° τ = 1 hr ; 3) the same, τ = 3 hrs ; 4) the same, τ = 6 hrs; 5) crustal part of crystallized glass heated at 610-620°, τ = = 12 hrs; 6) the same, τ = 72 hrs.

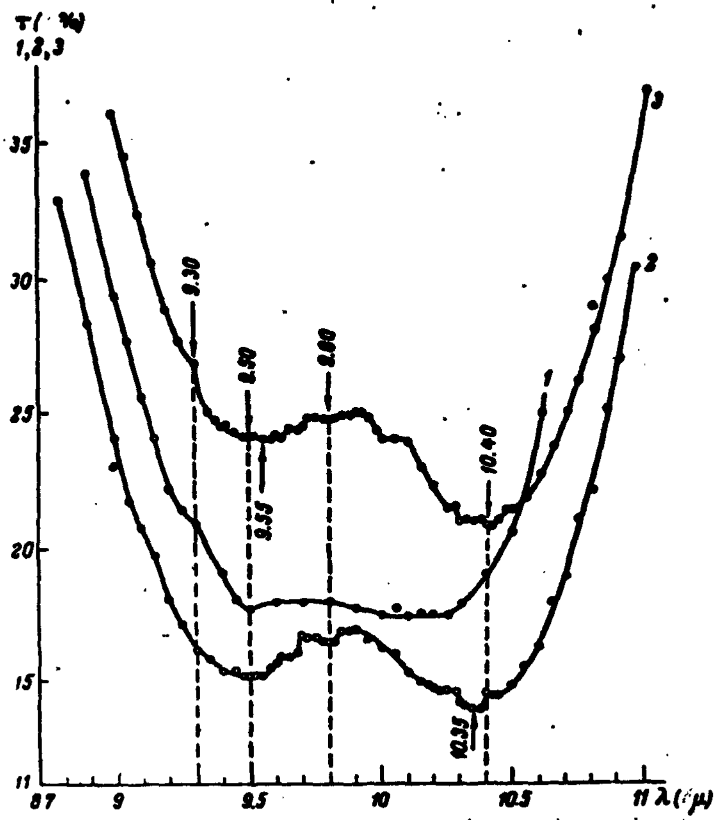

Fig. 7. Transmission spectra of film blown from a glass fusion having 30% Na_2O and 70% SiO_2 at various temperatures. 1) film blown from fusion at 1450°; 2) film blown from fusion at 1080°; 3) film blown from glass fusion of another melt.

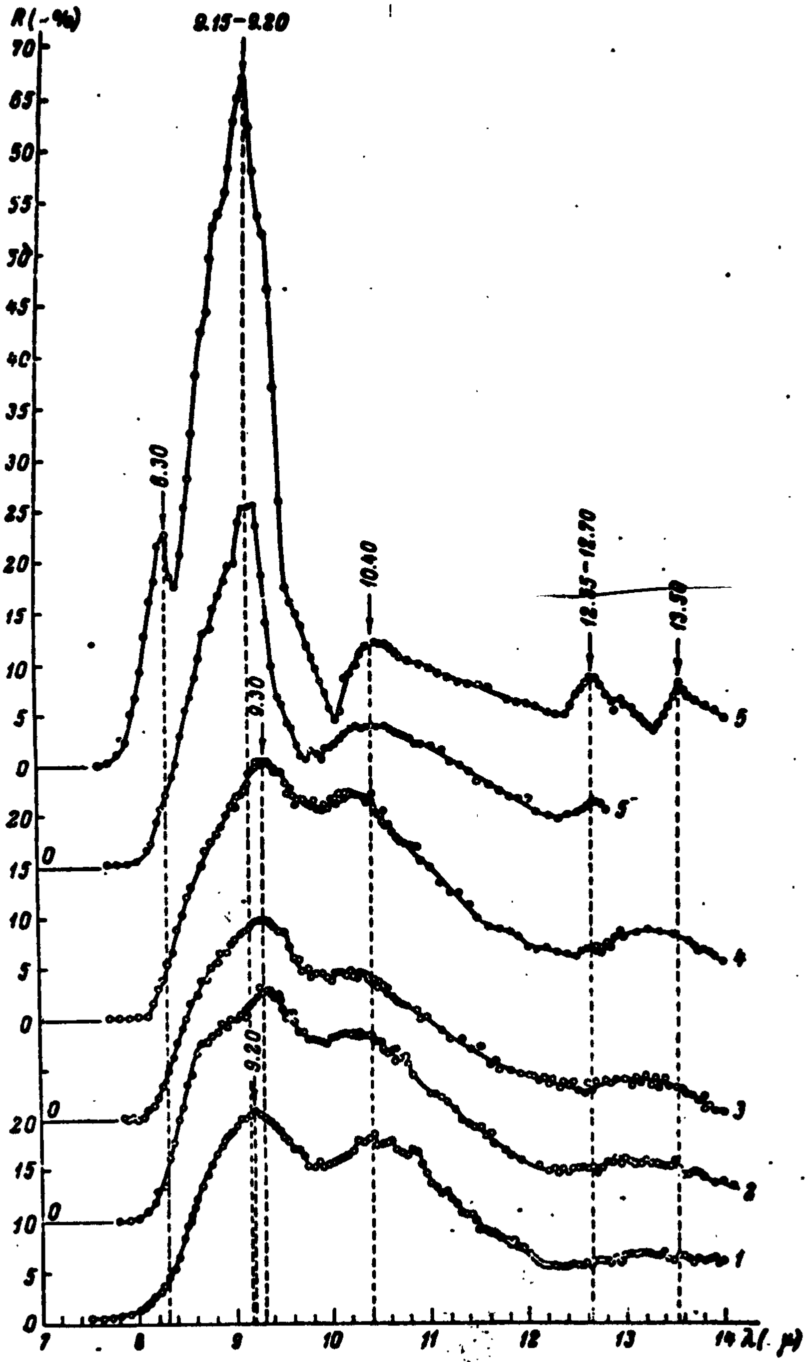

Fig. 8. Reflection spectra of glass with 25.5% Na_2O and 74.5% SiO_2.
1) first sample taken during early stage of fusion at 1450°; 2) the second sample taken an hour after the first at 1450°; 3) thirteenth sample taken after removing the pot at 1040°; 4) pot glass; 5) crustal part of glass heated 620° τ = 3 hrs; 6) crustal part of glass completely crystallized at 620°, τ = 60 hrs.

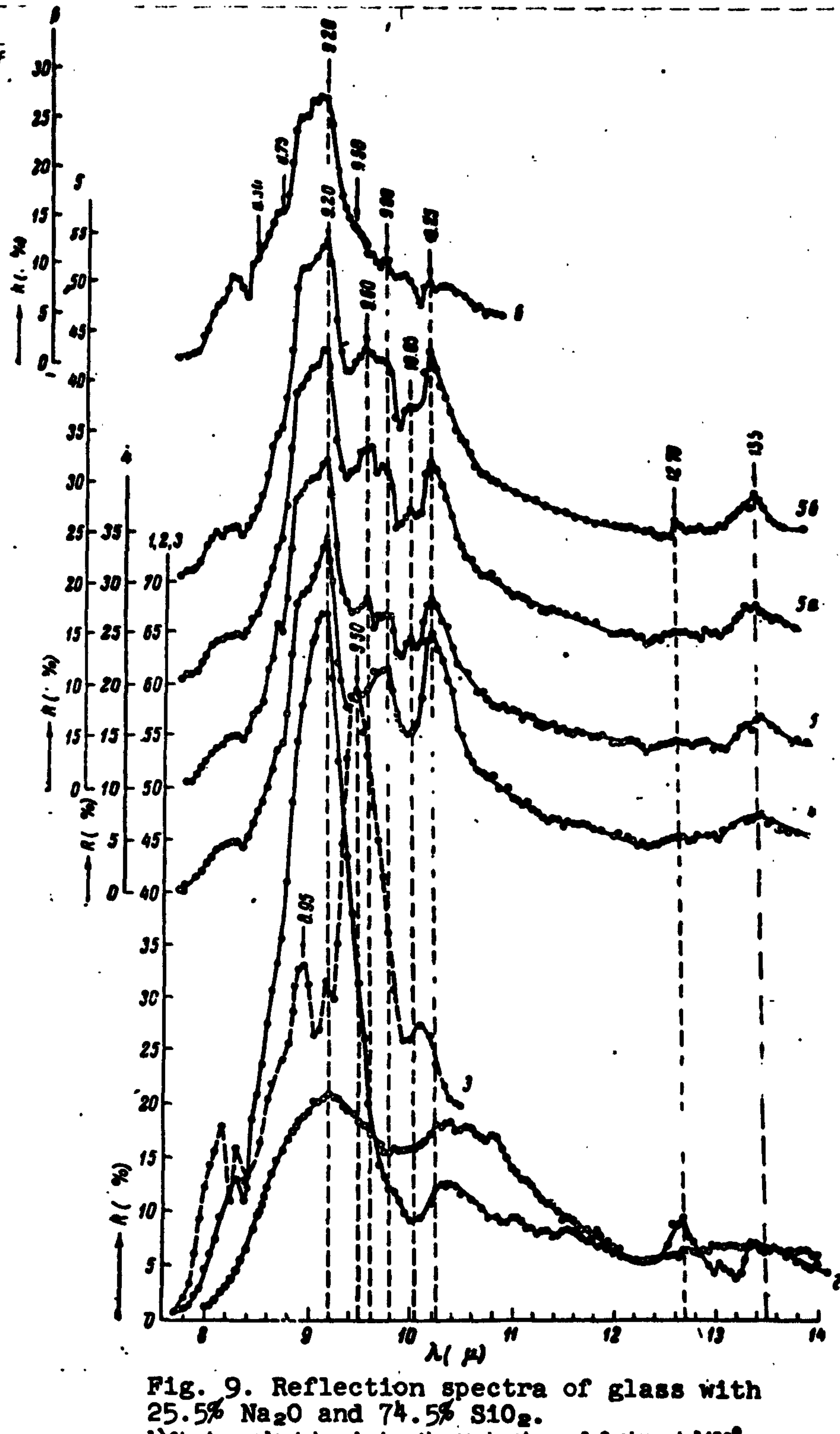

Fig. 9. Reflection spectra of glass with 25.5% Na_2O and 74.5% SiO_2.

1) first sample taken during the early stage of fusion at 1450°; 2) crustal part of the crystallized glass heated at 620°, τ = 576 hrs; 3) subcrustal part of glass crystallized at 620°, τ = 267 hrs; 4) the crustal part of glass crystallized at 260°, τ = 720 hrs; 5, 5a, and 5b) crustal parts of glass crystallized at 620°, τ = 1008 hrs; 6) crustal part of glass crystallized at 620°, τ = 1612 hrs.

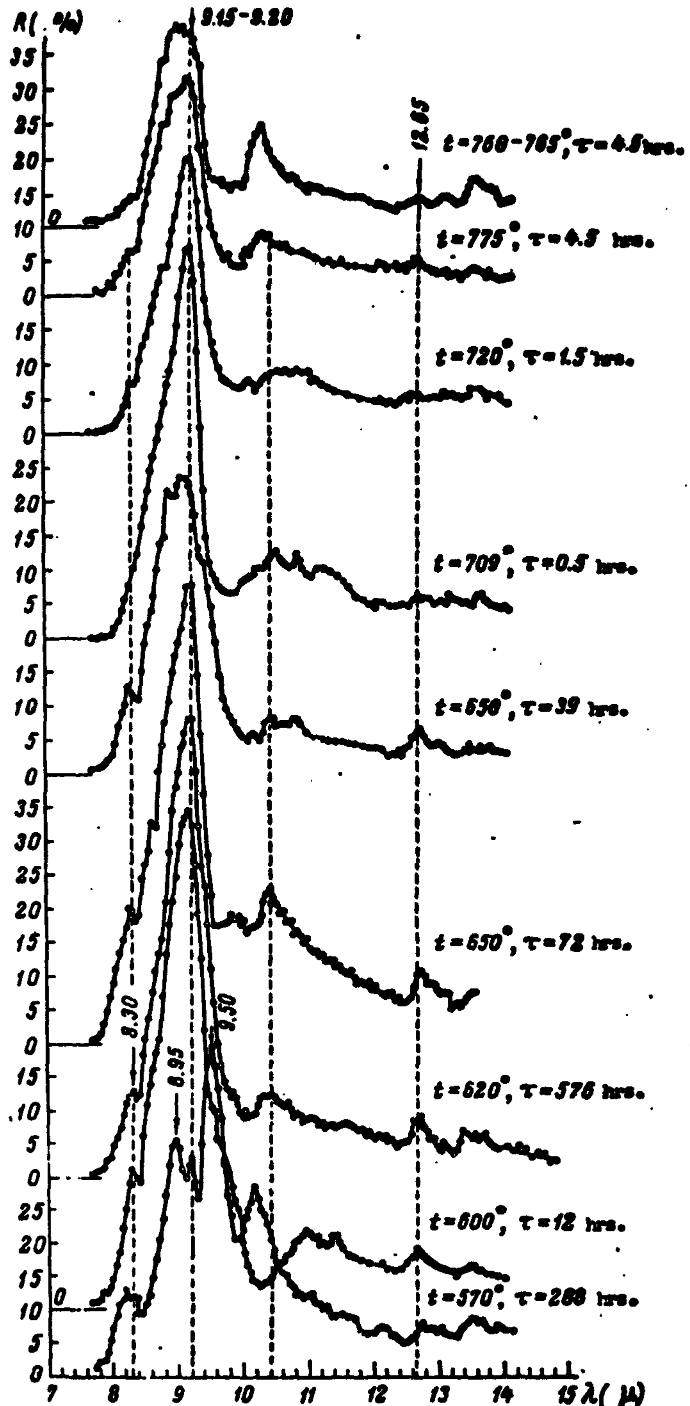

Fig. 10. Reflection spectra of crustal parts of glass with 25.5% Na_2O and 74.5% SiO_2 crystallized at various temperatures.

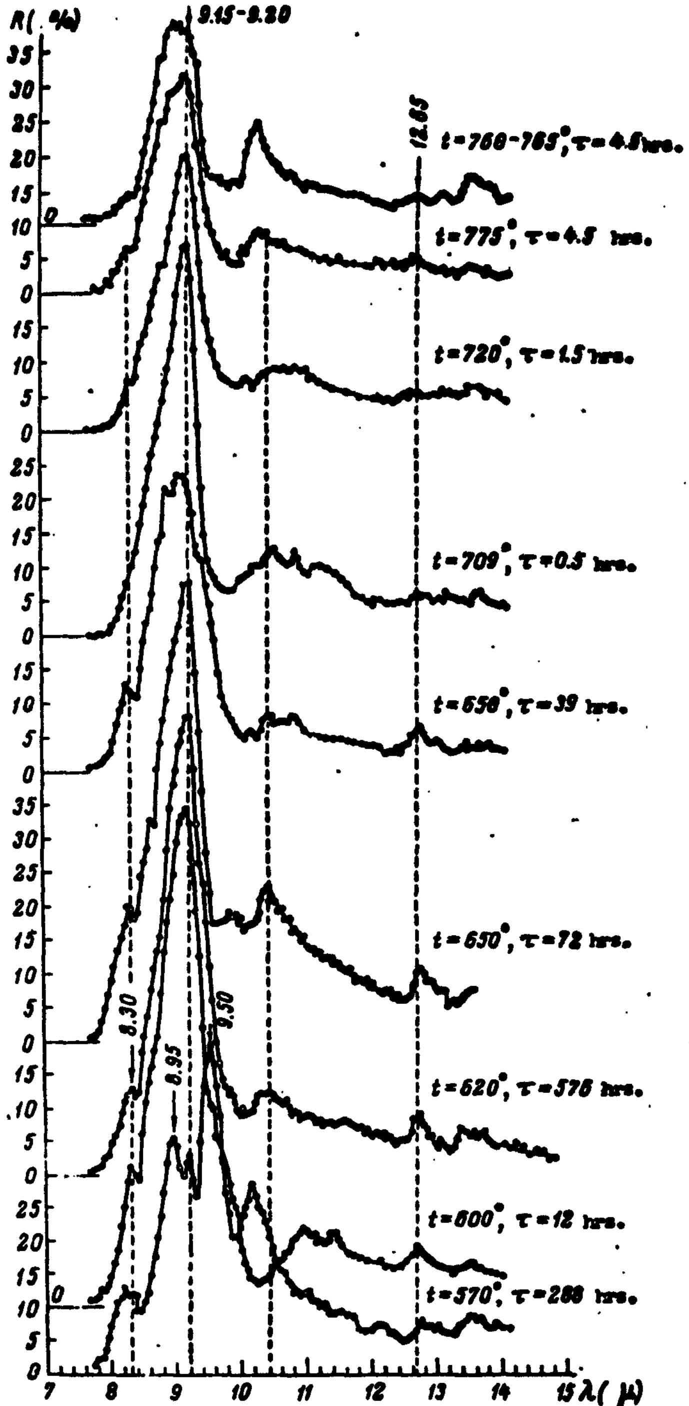

Fig. 10. Reflection spectra of crustal parts of glass with 25.5% Na_2O and 74.5% SiO_2 crystallized at various temperatures.

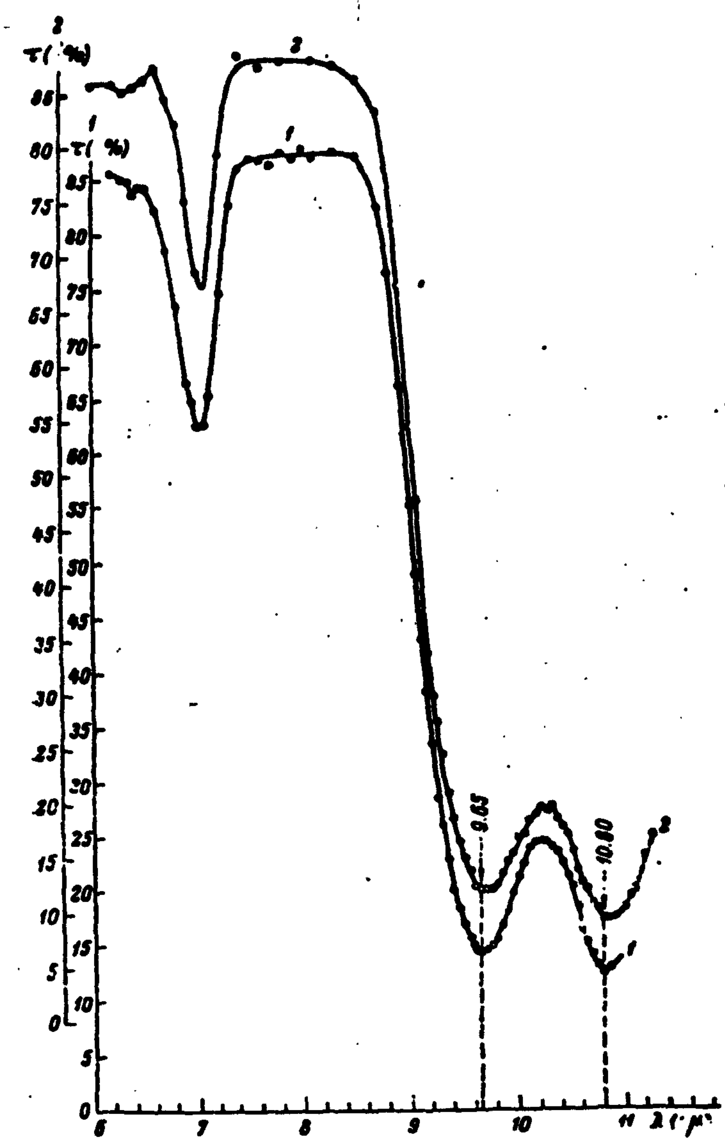

Fig. 11. Transmission spectra of glass blown from a glass fusion having 50% Na_2O and 50% SiO_2 in 22-liter quartz pots (different melt).

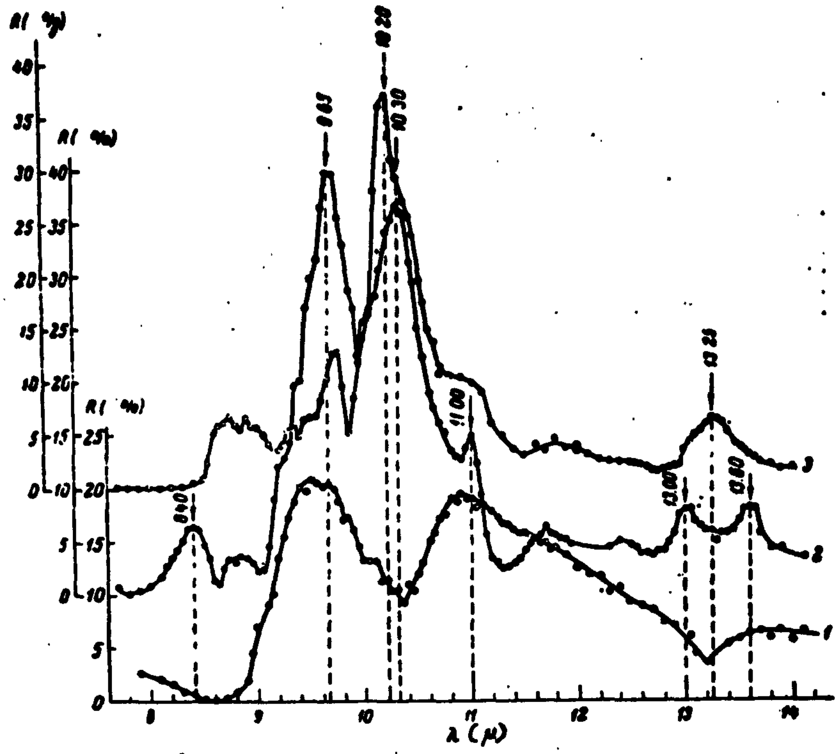

Fig. 12. Reflection spectra of glass with 50% Na_2O and 50% SiO_2 (melt No. 1810). 1) initial glass melted in a 22-liter quartz pot; 2) crustal part of glass completely crystallized at 600°, τ = 3.5 hrs; 3) crustal part of glass heated at 620°, τ = 144 hrs.

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EFFECT OF GLASS STRUCTURE ON SPECTRAL AND CHEMICAL PROPERTIES OF CERIUM IONS

G. O. Karapetyan

A number of authors [1-4] have investigated the spectroscopic properties of solutions, crystals, and glass containing cerium. In particular, interest in the investigation of cerium compounds has increased after an explanation was given of their important application in protecting glass from the coloring action of ionizing radiation [5-7], and also in connection with attempts to create luminescent screens using crystals activated by cerium [1, 5-7].

We will generalize the data concerning the investigation of the spectral-luminescent properties of glass activated by cerium.

Data have already been given concerning electron absorption and luminescence spectra [8,9], and also with respect to the absolute quantum yields of the luminescence [10] of glass containing cerium. Therefore, we have devoted primary attention to studying the effect of glass structure on the spectral and chemical properties of cerium ions.

The experimental method was described earlier [8-10]. It was pointed out [8,9] that cerium can exist in glass in tri- and tetravalent states. Moreover the absorption and emission bands of trivalent cerium in glass are connected with the permissible electron transitions for 4j and 5d. The absorption bands connected with the presence of tetravalent cerium are explained by electron transitions from oxygen ions, which make up the near environment, to tetravelent cerium ions. A change in the type of glass (phosphate, silicate, borate) strongly influences the cerium oxidation level, and leads to a qualitative rearrangement of the absorption and luminescence spectra.

The intensity of the trivalent cerium absorption band depends little on the glass composition, including the concentration of basic oxides. The position of the absorption band, however, changes significantly during transition from one type of glass to another (Fig. 1).

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We measured the absorption spectra of trivalent cerium in solutions and crystals in order to determine the cause of the changes occuring in the absorption spectrum of trivalent cerium when the glass composition changes.

Investigations of the absorption spectra of cerium salt solutions completely confirm the data given by other authors [1,2,5] (Fig. 1) and allow us to assume that the nature of the anion in the series Cl^-, SO_4^{--}, ClO_4^- does not affect the position of peaks.

The cerium absorption spectrum in the investigated monocrystals CaF_2, SrF_2, and BaF_2 has a weakly expressed structure (only a long-wave peak is sharply expressed) and though similar to the absorption spectrum of cerium in glass, sharply differs from the absorption spectra of cerium salt solutions (Fig. 2).*

A comparison of the absorption spectra of solutions, crystal, and glass shows that in crystals and glass the greatest intensity occurs in the longest wave band in the absorption spectra of trivalent cerium, while in solutions the intensity of the long-wave band in the absorption spectrum is negligible. Bands with peaks at 253 and 240 mμ have the greatest intensity in the absorption spectra of solutions containing trivalent cerium.

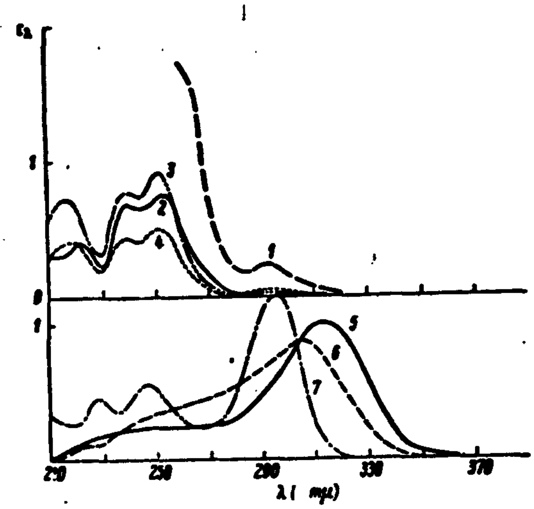

Fig. 1. Absorption spectra of solutions and glass containing trivalent cerium. 1) sulphate solution, 0.1% Cl; 2) the same, 0.02% Cl; 3) hydrochloric acid solution, 0.01% Cl; 4) the same 0.02% Cl (1-4 l = 10 mm); 5) glass $Na_2O \cdot 1.0\ CaO \cdot 5.0\ SiO_2$, 0.1% Cl; 7) the same $Na_2O \cdot 1.5\ CaO \cdot 2.5\ B_2O_3$, 0.1% Cl (5-7 l = 5 mm).

The disappearance and shift of separate bands in the cerium absorption spectrum and redistribution of intensity between short-

*Let me take the opportunity to express my deep gratitude to I. V. Stepanov and M. A. Vasil'yeva who cultivated the investigated monocrystals.

and long-wave peaks during transition from solutions to crystals and glass, which were observed with a change in the nature of the medium surrounding the cerium ions, are evidently connected with a decrease in the probability of the existence of excited stage levels which correspond to large electron transition energies (on transition from liquid to solid solutions) in which there is a stronger interaction between activator ions and the surrounding medium.

The stronger interaction of trivalent cerium ions with the medium in silicate glass as compared to phosphate glass is confirmed by the large half-width of absorption and luminescence bands, by smaller values of the quantum yields of luminescence, and by the more rapid onset of concentration quenching in silicate glass.

The dependence of the position of the cerium absorption bands on a change in the crystalline lattice parameters in the series of crystals CaF_2, SrF_2, and BaF_2 shows the effect of a change of the interaction strength of trivalent cerium with surrounding ions during stable coordination, inasmuch as it has been convincingly shown [11] that ions of the rare-earth elements isomorphicly replace calcium, strontium, or barium in these crystals.

Comparing ion radii magnitudes: Ce^{+3} – 1.18A, Ca^{+2} – 1.06A, Sr^{+2} – 1.27A, Ba^{+2} – 1.43A, it is apparent that isomorphic substitution of calcium in the fluorite lattice should lead to a significantly stronger cerium interaction with the surrounding medium than the isomorphic substitution of Sr^{+2} and Ba^{+2} in the SrF_2, BaF_2 lattices. Transition from a CaF_2 to SrF_2 lattice should cause qualitative changes in the cerium absorption spectrum. A transition, however, from an SrF_2 to BaF_2 crystal should have a relatively weak effect on the spectral properties of cerium, since the ion radius of both strontium and barium significantly exceeds that of cerium as opposed to the calcium ion radius. Thus, the obtained data confirm the concepts of the need for shifting the absorption bands toward the long-wave region of the spectrum with a decrease of the size of the nucleus occupied by a cerium ion, and also with its increased interaction with the surrounding medium.

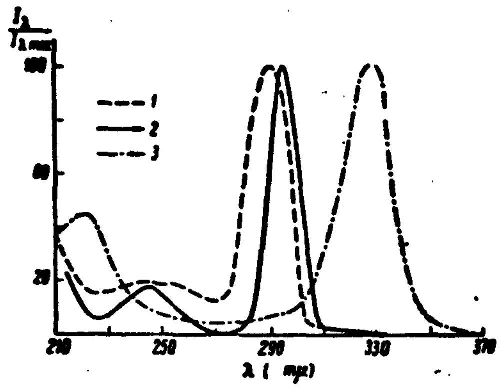

Fig. 2. Absorption spectra of crystals containing trivalent cerium.
1) $BaF_2 \cdot (Ce)$; 2) $SrF_2 \cdot (Ce)$; 3) $CaF_2 \cdot (Ce)$.

We should discuss separately the dependence of the intensity of the absorption bands of tetravalent cerium on the concentration of the basic oxides in glass. It has been shown that with increased concentration of the basic oxides in glass, the intensity of the absorption band of tetravalent cerium quickly increases. This is explained by the fact that because of the amphoteric nature of tetravalent cerium, and also the microheterogeneous glass structure [12], cerium can occupy a dual position in it (either in ionized sections, or in the structural lattice), which is connected with its discontinuity. In the first case the bond A—O—Cl occurs, where A is the alkaline or alkali-earth ion, and in the second case the bond B—O—Ce occurs where B is phosphorus, silicon, or boron. Evidently, such changes should greatly affect the intensity of the tetravalent cerium absorption band. The formation of these bonds in glass is similar to the formation of cerate in it.

In glass, evidently, the activator is always in some way distributed between the ionogenic and nonionogenic sections. When we increase the concentration of basic oxides in glass this equilibrium shifts and an additional number of activator ions goes into the ionogenic points.

Data concerning baorate, corosilicate, and other types of glass show that increasing the dimensions of the iogenic regions not only intensifies the tetravalent cerium absorption band but also makes the absorption band position less dependent on the nature of the glass-forming oxide.

In this paper we devote particular attention to a study of the effect of γ rays on glass activated by cerium. As is known, the action of ionizing radiation on glass leads to the formation of free electrons which are trapped by structural defects and extrinsic ions [13]. As a result, bands of additional absorption form in the ultraviolet and visible regions of the spectrum.

The introduction of cerium into glass does not change the nature of the bands of additional absorption which normally occur during irradiation of glass without cerium, but in this case the intensity of such bands significantly decreases. As a result, coloring of glass by ionizing radiation is significantly reduced and is completely prevented with large cerium concentrations.

The presence of intense luminesence of glass with cerium when exposed to γ-rays is very considerable [10]. The introduction of cerium into glass substantially affects the intensity and position of the thermoscintillation bands; moreover, the integral light sum magnitude passes through a maximum when the cerium concentration is increased. The optimum cerium concentration for the integral light sum is of the order of 0.25%. It should be noted that the optimum cerium content is 1-1.5% for luminescence at the instant of agitation as was shown using this same glass. This fact reflects the long-known principle that the optimum concentration for prolonged afterglow is always less that for temporary glow [14]. Cohn [15] observed a similar phenomenon in manganese-activated glass.

Deformation of the thermoscintillation band with an increase in the cerium concentration is explained by the fact that the optimum concentration of the activator is the lower, the higher the thermoscintillation temperature and hence, with a concentration increase, the maximum of the thermoscintillation band should shift toward the low-temperature side.

Variation of the dependence of the integral light sum on the cerium concentration shows that the introduction into glass of cerium in a concentration of even 0.1% reduces the intensity of the thermoscintillation band by more than half, which evidently was caused by a decrease in the number of capture centers. Decreasing the number of luminescence centers can also have significant importance if we assume that these centers energetically and structurally differ from corresponding electron and hole capture centers in the glass.

The quick decrease of the thermoscintillation band intensity with an increase of cerium concentration in the case of silicate glass corresponds to just as rapid an increase of the resistance of the glass to coloring by ionizing radiation.

Illumination of the irradiated glass with cerium by visible light causes a flash of luminescence. Investigation of the dependence of the luminescence intensity on the wavelength of the stimulating radiation showed that the greatest luminescence intensity can be obtained when the samples are illuminated in the 440 mμ region. In-just this region is located the maximum of the supplementary absorption band which is characteristic of silicate glass without activators [7]. When the irradiated glass is illuminated in the F-band, the intensity of the band decreases. Since the maximum of the absorption bands and luminescence of cerium are in the ultraviolet region of the spectrum, obviously, the action of the stimulating radiation is in no way connected with the immediate effect on the cerium ion and leads only to liberation of the electrons from capture centers of the basic substance. Radiation is characteristic for the presence of cerium ions and evidently has the same nature as after the luminescence which occurs immediately after cessation of irradiation.

Investigations of the spectral distribution of the scintillating action of light on the luminescence of cerium-activated glass, and its thermoscintillation very conclusively show that stimulated electrons are localized at levels of the so-called coloring centers, i.e., at levels conditioned by the thermal defects of the lattice and existing independently of an activator in the glass. Electrons which are liberated by optical or thermal methods can migrate in glass. Luminescence occurs after capturing the electrons at an orbit of the ionized trivalent cerium corresponding to the excited state.

As is known, irradiation of glass by ionizing radiation, in final analysis, always leads to the detachment of electrons from oxygen. When trivalent cerium is present in the glass, the oxygen ions make up the loss of electrons due to cerium, which leads to the emergence of ionized luminescence centers.

It should be noted that in the case of selective light absorption by the cerium ion itself, the electron evidently goes into an orbit corresponding to the excited state and either returns with radiation, or due to thermal energy, leaves the ion, which corresponds to the ionization of the centers of luminescence.

The proposed mechanism completely explains the presence of two luminescent processes in glass activated by trivalent cerium. In the first, which, according to terminology proposed by S. I. Vavilov [16], is spontaneous, there is immediate excitation of the centers of luminescence when ultraviolet rays are absorbed by trivalent cerium, and in the second, a recombination afterglow occurs due to capturing an electron from the conductance zone by an ionized center of luminescence. The screening effect of cerium, however, in relation to glass coloring during irradiation is explained not only by the fact that glass absorbs high-energy radiation which leads to ionization of trivalent cerium and to their subsequent capturing of free electrons from the conductance zone, but also by the fact that cerium, being an ion with different valences and having in the tetravalent state a great affinity to an electron, can capture electrons from electron capture centers located in its immediate vicinity, thus reducing the number of such centers.

An analysis of all the experimental data shows that in glass without additives recombination of electrons and holes is hampered since there are alkaline ions between the electrons and hole capture which are disposed neither to join with nor give off electrons. By introducing cerium into the glass it becomes possible to capture electrons and holes by cerium ions. Therefore the following processes occur during irradiation by ionizing radiation.

The oxygen ions, having lost electrons, capture them from trivalent cerium ions, and then the tetravalent cerium ions formed and present in the glass capture electrons both from the conductance zone and from the electron capture centers. The first process is accomplished by radiation, the second evidently occurs without it.

The simultaneous occurrence of these three processes when ionizing radiation acts on the glass is the reason for the decrease and, in a number of cases, even the complete prevention of coloring the glass with cerium during irradiation.

In conclusion I would like to thank V. V. Vargin and T. I. Veynberg for their guidance.

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ELASTIC PROPERTIES OF GLASS AS A FUNCTION OF TEMPERATURE

Ye. I. Kozlovskaya

We investigated the peculiarities of the deformation of silicate glass and materials of a mixed glassy-crystalline type as a function of temperature, nature of loading, its reaction time, etc.

Deformation was measured by static methods (twisting, with lever-indicator and optical measurement system, and bending) [1-2].

Figure 1 shows the dependence "strain-temperature" of glass twisted under conditions of a constantly acting load and a uniform temperature rise. T_g and T_f are, respectively, the softening point and the point of transition of glass into the liquid state. The magnitude of glass deformation does not change up to temperature T_g, but higher than T_g it increases rapidly in the 75-100° range; on subsequent heating, the deformation development slows down and the deformation curve assumes a direction parallel to the abscissa. We named this region of the curve the "deformation delay area", and the temperature point of the transition to this area has been designated T_z (the point that the deformation begins to delay). Above temperature T_f the deformation curve sharply increases — deformation develops as a rigid flow.

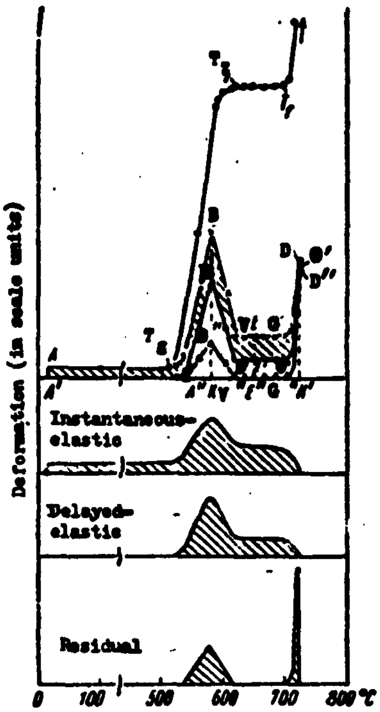

Fig. 1. The dependence "strain temperature" of glass.

The lower part of Fig. 1 shows an analysis of the deformation nature in temperature range – 20°-T_f. Curve ABVG indicates the magnitude of total deformation corresponding to each given temperature. It was obtained when the glass was heated in a no-load state with subsequent loading and unloading of the specimen every 100°, and in range T_g-T_f, every 25°.

Curve A'B'V'G'D' determines the boundary between instantaneous-elastic and delayed-elastic deformations, while curve A"B"V"G"D" is the boundary between delayed-elastic and residual deformations. The experimental points of the latter two curves were plotted as a result of reading the instantaneous-elastic and delayed-elastic recovery after removing the load.

The magnitude of each type of deformation at any temperature in range 20°–T_f is measured by segments of the corresponding ordinates enclosed between the boundary curves. Thus, only instantaneous-elastic deformation (AA') occurs in the range 20°–T. In the range T_g–T_z the magnitude of this deformation form at temperature K is segment BB'; the delayed-elastic deformation (segment B'B") and residual deformation (segment B"K) are at this same temperature. It is interesting to note that in the range of temperatures from T_z to T_f only elastic deformations (instantaneous-elastic and delayed-elastic) are observed.

On reaching T_f the elastic deformations (DD' and D'D") become barely discernible against the background of the quickly developing residual deformation D"K'.

In a previous article [3] we showed that the detected changes of glass deformation in various temperature ranges are also confirmed by data from determining the dependences "stress-strain" (hysteresis loop) and "strain-time" (yield curves). These data confirmed with complete clarity the peculiar elastic state of glass (with a significant amount of delayed-elastic deformation) in the region T_z–T_f. Under a small load the yield in this region is absent.

We observed the derived dependence of the elastic properties of glass on temperature for glass of varying chemical composition (Fig. 2). It is apparent from the diagram that this dependence was not typical only for fused quartz. The first noticeable increase in mobility of the fused quartz is observed at about 1100°. Plastic deformation commences above this temperature. There was detected no deformation delay and area formation on the deformation curve as a result of inattainment of an appropriate temperature (investigations were conducted to 1400°) or by virtue of the structural features of fused quartz.

The stated experimental material shows that the mechanical properties of glass heated above T_g change significantly.

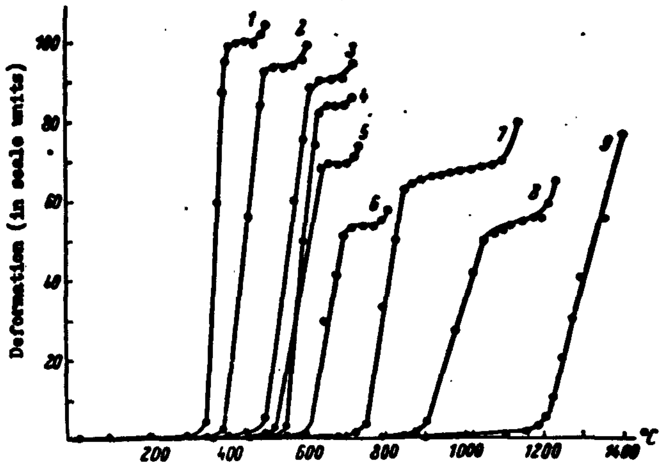

Fig. 2. The dependence "strain temperature" of glass and glazes of varying chemical composition. Glass: 1) TF-5; 2) TF-1; 3) window pane; 4) K-8; 5) BK-1; 6) TK-10; 9) fused quartz. Glazes for insulator porcelain; 7) 2 tssh; 8) 2.

These changes are undoubtedly connected with the structural changes of glass during the heating process. Generally, we can surmise the following concerning this connection.

It is known that cooling the silicate fusion decreases the thermal motion energy which results in decreased mobility of the particles, increased viscosity, and, in final analysis, fixed (frozen) structure characterized by high temperatures.

During heating, on the other hand, the thermal motion energy continuously reorganizes the mutual distribution of the particles.

In view of the X-ray diffraction analysis data concerning the invariability of glass structure from 20 to 400° [4] and the stability of the elastic properties of glass in this temperature range, we can assume that there is practically no change in the glass structure up to T_g. The glass remains here in a non-equilibrium energetically unstable "frozen" state. The relaxation time at these temperatures is so great that it has practically no noticeable effect on deformation change.

The transition of glass into a new kinetic state and its appropriate structural rearrangement occur only at temperatures higher than T_g. The particle oscillation energy reaches a magnitude here which leads to a weakening of the bonds and even to breaking of the weakest. The magnitude which determines the shift direction during particle regrouping is, to all appearances, the concentration gradient.

The endothermic effect on our thermograms of glass, corresponding to the range T_g–T_z, indicates that heat is absorbed when the structure rearranges. A rapid increase in the heat capacity of glass [5] is observed in this temperature range.

However, regrouping of the elements of the structure cannot follow the temperature change, since the relaxation time continues to be very significant as compared to the glass heating rate. Weakening of the bonds will lead to unit cell dissociation, to weakening of the whole frame-coordination lattice, and to distortion of it during loading; in this temperature range the glass is more capable of deforming.

Delayed elastic and plastic deformations become characteristic in conjunction with instantaneous-elastic deformation. We can judge this by the greatly increased hysteresis loop area and a change in slope of the principal axis of its ellipse, by the fact that the unloading branch does not return to zero, and by the "strain-time" curve which records the presence of the "material flow" [3].

At temperature T_z the relaxation time becomes less than the time for delivery of a corresponding amount of heat, and particle rearrangement no longer follows heat delivery — an energetically stable state sets in. Alkaline and other easily mobile ions occupy the equilibrium places inherent in their place in the fusion. The system becomes more rigid as compared to the inflexibility of the preceding structural rearrangement period in the range T_g–T_z and, under small loads, denotes an elastic state. The deformation curve forms a clearly expressed area. The hysteresis loop area decreases — the unloading branch slowly returns toward its original position. The heat reserve in this interval, however, is still insufficient to produce an equilibrium state of the elements of the silicic-oxygen skeleton itself.

The transition to a new and definitely structural-equilibrium glass state occurs at temperatures higher than point T_f.

Glass viscosity strongly decreases here — the glass changes into a liquid. Figure 3 shows deformation curves of samples made from mixtures of window glass with synthetic corundum pressed and roasted until agglutination; synthetic corundum is a crystalline phase in these two-phase mechanical systems. As the illustration shows, the mixture containing 60-80% glass and, correspondingly, 40 and 20% corundum repeated the characteristic features of deformation curve for clear glass. This means that the deformation character of such materials is determined by the properties of the vitreous phase. Deformation curves with a component ratio of 40:60% is less similar to the deformation curves of clear glass, and with a ratio of 20:80% suggests porcelain (chamotte) deformation curves which differ by the sloping characteristic of the deformation curve above point T_g and by the diffuse nature of the deformation delay area which, however, is noted in this case.

The nature of the elastic and plastic properties of glass which we established, especially the presence of the area T_z–T_f on the "strain-temperature" curves, in which glass flow which had begun at T_g temporarily ceases, can be, it seems to us, of great interest in the further development of the theoretical problems connected with the study of the structure of silicates in the vitreous state.

These observations can also probably be used when solving practical problems of the heat treatment of glass, in particular, fine heat treatment when obtaining new design materials with a glass base.

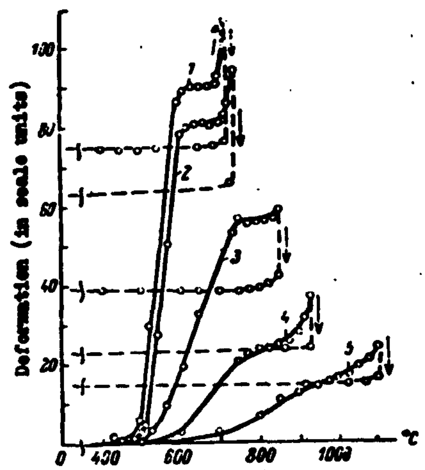

Fig. 3. The dependence "strain-temperature" of glass-corundum compositions. 1) clear glass; 2-5) glass mixtures with 20, 40, 60, and 80% powdered corundum respectively (solid line is heating with loading, dashed line is cooling without loading).

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